

Effects of Processing and Cooking on PBB Residues

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To study the effect of processing on polybrominated biphenyl (PBB) levels, milk from four dairy herds containing less than 0.3 ppm (fat basis) of physiologically incorporated PBBs was processed individually into cream, skim milk, butter, and stirred curd cheese. Pasteurized and freeze-dried whole milk, skim milk, and cream, spray-dried whole milk and skim milk, and condensed whole milk were also made. PBBs were concentrated in the high-fat products. Spray-drying reduced PBBs in whole milk and skim milk while pasteurization, freeze-drying, aging of cheese, and condensation were not effective.

To study the effect of cooking on PBB levels, thigh meat, thigh skin, drumstick and breast (with skin) from half of chickens fed PBBs were analyzed raw, and pieces from the other halves were analyzed following separate pressure cooking. The level of PBBs expressed as parts per million on a solids basis was lower in the cooked sample than in the corresponding raw piece and part of the PBBs lost were found in the drip. Recoveries of PBBs in cooked tissue and broth ranged from 68.1% in the thigh skin to 84.6% in the drumstick, with approximately two-thirds of the recovered PBBs found in the cooked meat itself. Therefore, pressure cooking resulted in a loss ranging from 36% for the drumstick to 53% for the thigh skin.

Introduction

Polybrominated biphenyls (PBBs) were mistakenly used in place of magnesium oxide in dairy feeds in Michigan in May, 1973 (1). Subsequent cross feed contamination led to their occurrence in milk and eggs as well as meat of beef, swine, sheep, and poultry. Although precise information concerning toxicity of PBBs at very low levels is not known, research was initiated to assess the possibility of reducing PBBs by processing and cooking because of possible chronic effects of continued assimilation and accumulation of these compounds in body fat.

Processing and cooking have been found to have some potential for reducing levels of chemically similar compounds such as the chlorinated hydrocarbon pesticides and polychlorinated biphenyls. Condensation has shown to be effective in the reduction of telodrin in milk (2), freeze-drying significantly reduced lindane, dieldrin, *p,p'*-DDT, and *o,p'*-DDT-DDD from whole eggs (3), heating skimmed milk decreased PCB residues (4), and

spray-drying promoted losses of chlorinated hydrocarbon pesticides (5, 6). Cooking has reduced these lipophylic compounds from such products as poultry (7-11), sausage patties (12), bacon (13), pork loins (14), pork muscles (15) and beef loaves with texturized soy (16). Most of the losses were attributed to fat rendering or leaching out during cooking—the more severe the rendering the greater the loss. Different levels of success in elimination of the contaminants were found depending upon the compound studied, the levels of contamination and the tissue from which the extraction was accomplished.

Methods

Processing

Milk with less than 0.3 ppm (fat basis) was obtained from four dairy herds identified by the Michigan Department of Agriculture. The milk from each herd was separated into cream and skim milk fractions followed by pasteurization of the whole milk and skim milk at 62.8°C/30 min and cream at 71.1°C/30 min. Cream was churned in an institutional mixer to make butter. A stirred curd Cheddar type cheese was made from pasteurized whole milk following the procedure of Kosikowski (17). Por-

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tions of the pasteurized cream, whole milk, and skim milk were placed in freeze-drier trays giving a depth of approximately 6.5 mm (1/4 in.) and frozen overnight at -23°C. These were further freeze-dried in a Virtis REPP freeze-drier, model FFD42 WS, for 24-30 hr with a system pressure of 5×10^{-3} torr. The temperature of the platen was 65.6-71.1°C, giving a final product temperature of 48.8-51.6°C. Milk from two herds was spray-dried and condensed. The pasteurized whole milk of each herd was prewarmed to 54.5°C and then condensed in a research model Rogers vacuum pan to approximately 35% solids. Pasteurized whole milk and skim milk were heated to 48.8°C and spray-dried by using pilot plant equipment with an air outlet temperature ranging from 76.6 to 98.8°C.

Pressure Cooking

Fifteen White Leghorn hens, approximately 9 months of age, were fed a standard cage layer ration for 5 weeks which was contaminated with 0, 30, 45, 60, and 90 ppm FireMaster FF-1 (three hens/feeding level). At the end of 5 weeks the first three groups (0, 30, and 45 ppm levels) were slaughtered. The remaining two groups were placed on clean feed for an additional 8 weeks and then slaughtered. The hens were picked, eviscerated, and chilled overnight in ice water before being carefully dissected to provide breast pieces, drumsticks, thigh meat, and thigh skin from the right side for raw analyses and those from the left side for cooking and subsequent analyses of cooked meat and broth. A 3.8 liter aluminum pressure sauce pan was used to pressure-cook each piece separately for 15 min under 15 psi in 500 ml deionized water.

Analyses

PBBs were extracted and cleaned-up in duplicate by using the general AOAC procedure for chlorinated hydrocarbon pesticides (18). Moisture and lipid determinations were carried out in duplicate by drying at 100 and 70°C, respectively, under vacuum of 711 mm. Lipid samples were evaporated, and aliquots of the petroleum ether extracts used for PBB analyses.

Gas chromatographic analyses were carried out by using a Tracor 560 GLC instrument equipped with a ⁶³Ni electron-capture detector and interfaced to a Digital PDP-8-Pamila GC data system. The column for GLC was a Pyrex column, 1.83 m long \times 4.0 mm id, packed with 3% OV-1 on Chromosorb W 80/100 mesh HP. The carrier gas was nitrogen with a flow rate of 40 ml/min. Temperatures at the injection port, column, and EC detector were 270, 240,

and 300°C, respectively. Standard PBB (FireMaster BP-6, lot No. 5143, Michigan Chemical Corporation, Chicago, Illinois) solutions were prepared in petroleum ether and injected at the beginning of each run, after every five or six samples, and at the end of the run. Quantitations were based on the peak area of the standards (hexabromobiphenyl peak). PBB residues were confirmed by ultraviolet spectral and mass spectrometric analyses.

Results and Discussion

Processing

The lipid content and levels in the raw milk and in most of the manufactured products are shown in Table 1. Examination of PBB levels on a wet weight basis in the total sample shows that the PBB concentration follows the fat in these dairy products. Analysis of variance revealed the PBB contents (fat basis) of these products were not significantly different. Pasteurization appeared to reduce slightly the PBB content of the whole milk and cream. Pasteurization has been reported to have very little effect on the DDT levels in milk (19). Skim milk, buttermilk, and cheese whey contained slightly higher PBB levels than did pasteurized whole milk, per fat unit, suggesting some PBB may be associated with lipoprotein and/or may be soluble in the serum of milk. This nonproportionality to the fat content has previously been observed (6) in studies with several chlorinated hydrocarbon pesticides. The freeze-dried whole milk and cream showed slightly higher PBB contents than the pasteurized whole milk and

Table 1. Lipid content and PBBs in milk and related dairy products.

| Products | Lipid content, % | PBBs, ppm | |
|-------------------------|------------------|--------------|-------------|
| | | Total sample | Lipid basis |
| Raw whole milk | 4.5 ^a | 0.009 | 0.20 |
| Pasteurized milk | 3.9 | 0.006 | 0.15 |
| Raw skim milk | 0.3 | 0.000 | 0.11 |
| Pasteurized skim milk | 0.2 | 0.000 | 0.16 |
| Raw cream | 29.7 | 0.054 | 0.17 |
| Pasteurized cream | 32.3 | 0.060 | 0.16 |
| Butter | 73.8 | 0.108 | 0.14 |
| Buttermilk | 0.7 | 0.001 | 0.18 |
| Fresh cheese | 28.6 | 0.051 | 0.18 |
| Aged cheese | 27.9 | 0.044 | 0.17 |
| Cheese whey | 0.6 | 0.001 | 0.18 |
| Freeze-dried whole milk | 26.1 | 0.054 | 0.20 |
| Freeze-dried skim milk | 0.8 | 0.001 | 0.08 |
| Freeze-dried cream | 80.0 | 0.146 | 0.18 |

^a Based on duplicate determinations from each of four herds.

cream, but these results were primarily due to extraneous interfering peaks present only in the freeze-dried products. Aging of Cheddar cheese for approximately 2 months showed very little effect on the PBB levels. Condensation was not effective in the removal of the PBBs from whole milk.

Significant differences ($p < 0.05$) were found among high-fat and low-fat content products when the PBB levels were expressed on a total weight basis. Butter, cheese, and freeze-dried cream had higher PBB levels than buttermilk, cheese whey, and cream, respectively, reflecting the preferential distribution of PBBs in the lipid phase of the products.

Spray-drying appeared to promote losses of PBBs from whole milk and skim milk at the specified conditions (Table 2). Significant losses of PBB of approximately 30–36% from whole milk and 61–69% from skim milk of herd 2 were observed. Although the levels in the spray-dried products from herd 1 were less than the levels in the pasteurized products, the differences were not significant.

Losses of PBB from the spray-dried skim milk (61–69%) were greater than from the spray-dried whole milk (30–36%). These results suggest that PBBs were more easily removed from low-fat content products and/or when the levels in the original product were low. It is possible that some PBB is distributed in the serum phase of milk and that this quantity could be more easily removed than the PBB associated with the lipid phase. Moreover, the greater surface area formed during spray-drying of the liquid product and the relatively high temperature at which the formed particles are exposed could facilitate the volatilization of the PBBs.

Table 2. Effect of spray-drying on the PBB residue contents of pasteurized whole milk and skim milk (based on lipid content)^a

| Herd | Product | PBB residue, ppm ^a | | <i>t</i> statistic |
|------|------------|-------------------------------|-------------------|--------------------|
| | | Liquid ^b | Spray-dried | |
| 1 | Whole milk | 0.26 | 0.22 ^c | 4.29 |
| | Skim milk | 0.23 | 0.34 ^d | -2.28 |
| | Skim milk | 0.23 | 0.06 ^e | 3.80 |
| 2 | Whole milk | 0.15 | 0.09 ^f | 7.36 ^g |
| | Whole milk | 0.15 | 0.11 ^h | 16.48 ^g |
| | Skim milk | 0.21 | 0.08 ^h | 7.21 ^g |
| | Skim milk | 0.21 | 0.07 ^h | 92.5 ⁱ |

^a Values are an average of two determinations.

^b PBB residue content of original product.

^c Air outlet temperature: 87.8°C.

^d Air outlet temperature: 76.6°C.

^e Air outlet temperature: 87.8–93.3°C.

^f Air outlet temperature 85–90.5°C.

^g Significant at the 5% level of probability.

^h Air outlet temperature 87.8–98.8°C.

ⁱ Significant at the 1% level of probability.

Pressure Cooking

When the chicken pieces were pressure-cooked, the level of PBBs in the wet tissue decreased slightly (Fig. 1). Part of the PBBs lost was recovered in the broth. The level of PBBs in the broth of breast pieces was higher than that in the broth of the other pieces. Since the amount of cooking water was constant, greater amounts of PBBs in the breast broth resulted from a larger amount of fat rendered from the larger piece.

Since rendering of fat is the major mode of removal of these lipophylic compounds, PBBs were also expressed on a fat basis (Fig. 2). Average values in the fat of cooked pieces were slightly higher than those in the fat of the raw pieces. Thus, while rendering of fat is undoubtedly an important mode of PBB reduction, the amount of PBB reduced is not directly proportional to fat removed.

Total weights of PBBs in the cooked chicken and broth were compared to the level in the respective raw chicken piece to calculate the percentage recovery. No significant differences occurred among the percentages of PBB recovered in any of the four pieces; percentage recoveries were 68.1% in thigh skin, 75.8% in the breast piece, 83.9% in the thigh meat, and 84.6% in drumsticks. Recoveries, however, did tend to be higher in the chicken pieces which contained less fat (i.e., drumstick and thigh meat) even though these pieces had lower per-

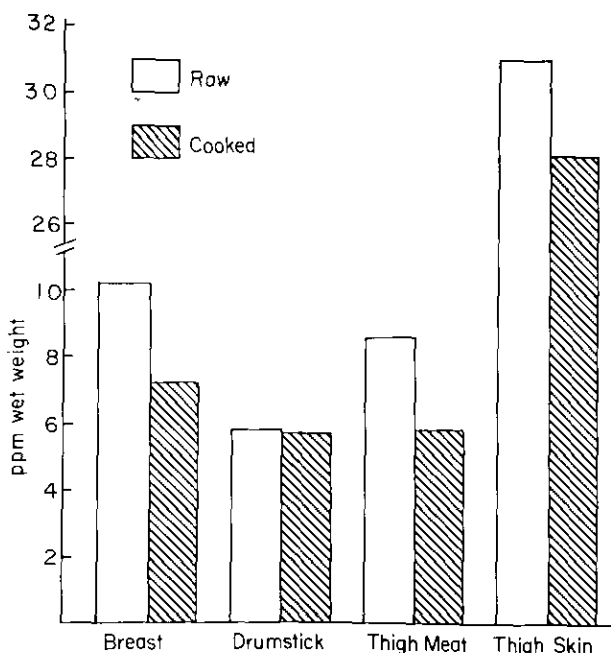


FIGURE 1. Level of PBBs expressed on a wet weight basis in raw and cooked chicken pieces.

tage meat yields than did the higher fat breast piece or thigh skin.

The percentage of recovered PBBs in the meat did not differ significantly among the four pieces evaluated and ranged from 65.5% in the cooked thigh skin to 72.9% in the cooked drumstick (Fig. 3). The distribution of the recovered PBBs between the cooked meat and broth is illustrated in Figure 4. The proportion of the recovered PBB in the cooked meat is considerably higher than that found in previous studies. Recovered PCBs were about equally distributed between the cooked meats and broth (7), while only $\frac{1}{4}$ to $\frac{1}{3}$ of recovered lindane, dieldrin, and DDT compounds occurred in the cooked hen pieces (8). The bulkier size and higher molecular weight of the PBB molecules may contribute to a smaller proportion of the recovered material being found in the broth. Moreover, Stadelman et al. (20) reported that feeding high levels of several pesticides resulted in greater residue persistence in eggs and abdominal fat of hens than was found when low levels were fed. Thus, the high levels of contamination may have influenced this distribution. For pieces from control hens with 0.02 to 0.07 ppm (wet basis) of PBB, the proportion of recovered PBBs in the meat was slightly less, ranging from 39.8% in the drumstick to 52.7% in the thigh meat.

Considering ingestion of the cooked meat only, pressure cooking brought about a total loss of PBBs from that which occurred in the raw meat of 44% for the breast piece, 36% for the drumstick, 42% for the thigh meat, and 53% for the thigh skin.

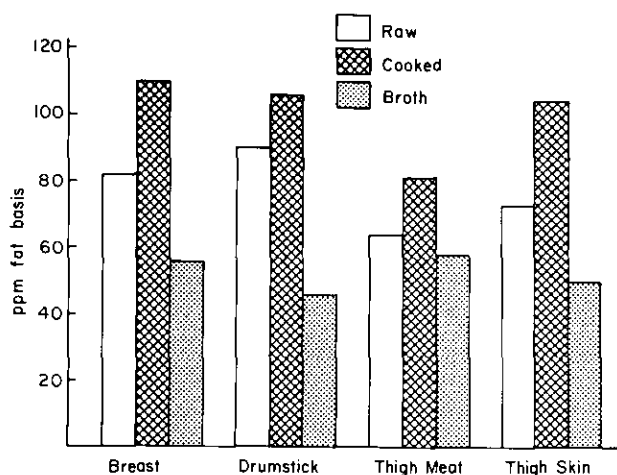


FIGURE 2. PBBs in the fat of raw and cooked chicken pieces and chicken broth.

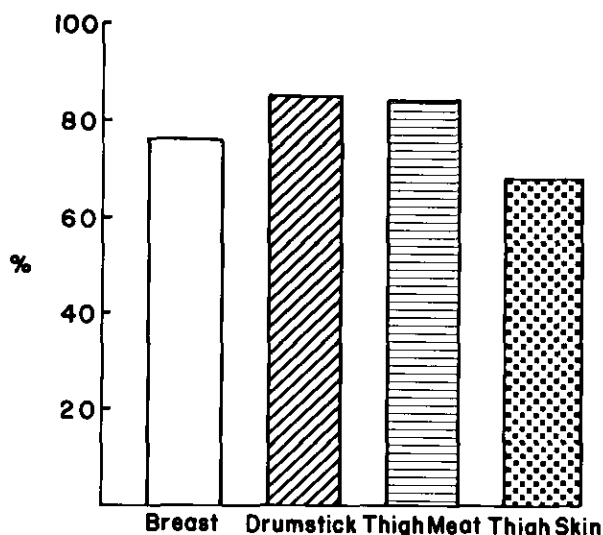


FIGURE 3. Percentage recovery of PBBs in combined cooked chicken pieces and broth based on level in raw pieces.

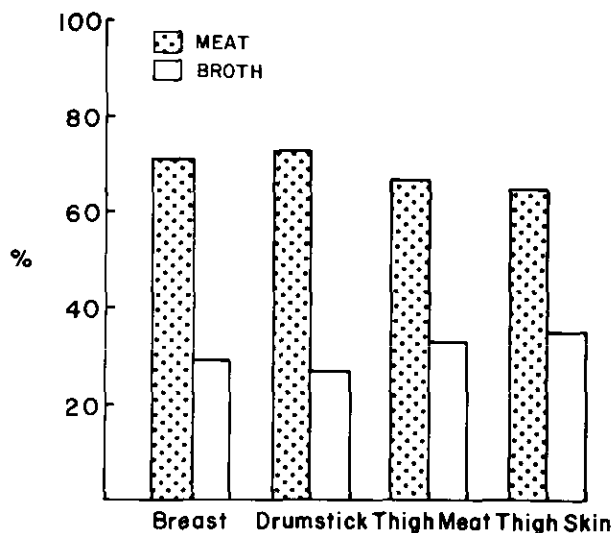


FIGURE 4. Distribution of recovered PBBs between the cooked piece and the chicken broth.

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